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Kinetic study of the hydrogenolysis of polychlorobenzenes over a Pd/C catalyst in an alkaline aqueous-*n*-hexane system

Iwona Anusiewicz [a], Tadeusz Janiak [a,*], Janina Okal [b]

[a] *University of Gdańsk, Faculty of Chemistry, J. Sobieskiego 18, 80-952 Gdańsk, Poland*
[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland*

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ABSTRACT

The kinetics of the hydrogenolysis of chlorobenzene, dichlorobenzenes and some trichlorobenzenes over a 10% Pd/C catalyst was studied using a multiphase system. The reactions were carried out in a batch reactor with an aqueous NaOH/*n*-hexane solution of chloroaromatic compound as the liquid phase. Benzene was the final product of the hydrogenolysis of all the compounds studied. Hydrogenolysis was more effective in the presence of *in situ* generated hydrogen than gaseous hydrogen. The initial reaction rates and TOFs of dichlorobenzenes and trichlorobenzenes were slightly lower than those of chlorobenzene. The position of the chlorine atoms in trichlorobenzenes affects the kinetics of the removal of the first chlorine from these molecules. The differences in chlorine reactivity were explained by the inductive and steric effects induced by the benzene-Cl bonds.

1. Introduction

Organochlorine compounds, being persistent pollutants, are of great environmental concern; therefore, wastes containing them should be properly treated before final disposal to avoid further unnecessary contamination of the environment [1,2]. One possible, promising solution to this problem is to convert aromatic chlorides to dechlorinated compounds by hydrogenolysis [2] and to use the product as a fuel. Hydrogenolysis of organohalogen compounds has been investigated using different reducing reagents, catalysts and substrates [2,3]. The usual aim of the procedures described in the literature [2–5] is to convert a particular organochlorine compound to the desired reaction product. For example, in the Rosenmund reduction, acid chlorides are converted to aldehydes without further reduction to alcohols [4]. But in the treatment of hazardous wastes, it is effectiveness of halogen removal and simplicity of the reaction system that are in fact required. The hydrodechlorination of chloroaromatic compounds is known to proceed over various transition metal catalysts [2,4,5]. In particular, Pd, Rh and Pt supported on carbon, alumina or Raney nickel have been reported to promote hydrogenolysis of the carbon–chlorine bond [2,3,6,7]. Palladium on activated carbon appears to be the catalyst of choice [5], and to the best of our knowledge, it is indeed the most effective in hydrodechlorination. Dechlorination in the presence of supported Pd has been studied in the gaseous [8–14] and liquid phases [15–29]. Heterogeneous multiphase liquid systems appear to be useful in the treatment of wastes containing chloroaromatic constituents. There are reports that the hydrogen chloride produced during the hydrodehalogenation of organochlorine compounds deactivates the catalyst surface [9,26]. However, in liquid multiphase heterogeneous catalytic hydrogenolysis a base is easily added to restore catalyst activity by reacting with the hydrogen chloride [23–26]. Moreover, aqueous and nonpolar phases facilitate desorption of both hydrogen chloride and dechlorinated compound from the catalyst surface, each one to a different phase.

Although hydrogenolysis of aromatic chlorides with gaseous hydrogen is far from uncommon, the available literature data on the kinetics of the process in the liquid multiphase system are rather sparse; the most comprehensive reports in this respect are those of Marques et al. [21,22] and Janiak et al. [24–26]. Recently, we investigated the kinetics of the hydrogenolysis of o-chlorotoluene [25] and some meta-substituted chlorobenzenes [26]. Generally, we found that in meta-substituted chlorobenzenes the effectiveness of chlorine removal does not depend essentially on the type of substituent [25,26].

In the present work we studied the kinetics of the dechlorination of mono, di and some trichlorobenzenes in a multiphase system in the presence of a 10% Pd/C catalyst. In particular, we investigated how the number of chlorine atoms in a molecule and their position in polychlorobenzenes influences the susceptibility of these heteroatoms to dechlorination. There are few data on the hydrogenolysis of dichlorobenzenes [10,14,26] and trichlorobenzenes [28,30,31] in the literature, in contrast to the hydrogenolysis of monochlorobenzene [9–11,14,15,17,23,24,28]. The hydrogenolysis of 1,2,4-trichlorobenzene, as well as 1,2,3,4- and

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[*] Corresponding author. Tel.: +48 58 523 53 21; fax: +48 58 523 53 57.
E-mail address: janiak@chem.univ.gda.pl (T. Janiak).

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1,2,4,5-tetrachlorobenzene was investigated in a fixed bed circular reactor over a supported Pd catalyst and hydrogen gas [30]. The hydrogen transfer hydrogenolysis of 1,2,4-trichlorobenzene was also studied over a Rh/C catalyst [28]. In the gaseous phase, the hydrogenolysis of 1,2,4-trichlorobenzene and 1,2,4,5-tetrachlorobenzene was investigated in the presence of a Ni–Cr catalyst [31]. Despite these efforts, however, there is some uncertainty surrounding the relation between carbon–chlorine reactivity and the position of chlorine in polychlorinated benzenes.

We also carried out a number of experiments to improve the effectiveness of our hydrogenolysis system using chlorobenzene as a model compound: for example, we wanted to see how the addition of 2-methoxyethyl ether or 2-methoxyethanol affects the hydrogenolysis reaction. Generally, these solvents are totally miscible with water at room temperature, and totally (2-methoxyethyl ether) or partially (2-methoxyethanol) miscible with *n*-hexane. Both compounds are non-ionic surfactants, strongly adsorbing on polar-nonpolar interfaces and modifying (lowering) the corresponding surface tension values. It was found that these substances may improve the hydrogenolysis of chloroaromatic compounds [32]. The effectiveness of hydrogenolysis with gaseous and *in situ* generated hydrogen was also investigated. This is a novel, innovative contribution in this field.

2. Experimental

2.1. Materials and chemicals

10% Pd/C catalyst, *n*-hexane (99%, HPLC), 1,2-dichlorobenzene (99%), 1,3-dichlorobenzene (99%), 1,4-dichlorobenzene (99%), 2-methoxyethanol (99.3%), 2-methoxyethyl ether (99%) and aluminium granules (99%) were from Aldrich. Benzene (99%) and m-xylene (99%) were supplied by POCH Gliwice (Poland), while 1,2,3-trichlorobenzene (99%) was from Fluka and 1,2,4-trichlorobenzene (99%) from BDH (England). All reagents and solvents were used without further purification.

2.2. Apparatus and procedures

The hydrogenolysis reactions were carried out in a 50 ml thermostatted three-necked round-bottomed flask at 20 °C. Gaseous hydrogen was introduced by gas burette at atmospheric pressure. In a typical hydrogenolysis procedure, 100 mg of the 10% Pd/C catalyst was first pre-treated by soaking it in 10 ml of an *n*-hexane solution of 2.45 mmole of chlorinated compound and 0.25 mmole m-xylene (internal chromatographic standard), after which 15 ml 10% aq NaOH was added. The reactor was flushed twice with hydrogen and the mixture magnetically stirred at 1300 rpm with a 12 × 5 mm stirring bar. The instant the stirrer was turned on was taken to be starting point of the reaction. The hydrodechlorination was also conducted with the addition of 2-methoxyethanol or 2-methoxyethyl ether (diglyme) (0.6 ml), which were added with the *n*-hexane.

The hydrogenolysis reaction, with hydrogen generated *in situ* by the reaction of Al granules with aq NaOH in the reaction flask, was performed in the same apparatus. First, the flask containing the reagents as above was flushed with nitrogen, then 0.07 g Al granules was added and the reactants stirred at the same rate as above. The gas burette served as a buffer gas holder to store the surplus of hydrogen generated.

2.3. Analyses

The course of all the hydrodechlorination reactions was monitored by measuring hydrogen consumption and also by sampling and analysing the *n*-hexane layer. In all experiments, on completion of H_2 uptake, the reaction mixture was filtered and separated into to the aqueous and *n*-hexane layers. Chloride anions were analysed in the aqueous layer (by the Volhard method) and the hydrogenolysis products in the *n*-hexane layer. The analyses were performed on a PYE Unicam 104 gas chromatograph equipped with a flame ionisation detector (FID) and packed columns. Analyses of the *n*-hexane layers were preceded by a test to evaluate the accuracy and precision of the chromatographic method. In this test, 15 ml 10% aq NaOH, 100 mg 10% Pd/C and 10 ml of an *n*-hexane mixture containing known quantities of 1,2,3-trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, chlorobenzene, benzene and m-xylene (as internal standard) were stirred in the reactor. The *n*-hexane layer was then analysed by gas chromatography. The accuracy of these chromatographic assays was 5%. The precision of the chromatographic assays of the hydrogenolysis products was better than ±8%, and that of the chloride ion was better than ±0.2%.

3. Results and discussion

The commercial 10% Pd/C catalyst was previously well characterised by different techniques [26]. Prior to characterisation the catalyst was treated in a stream of hydrogen at 400 °C for 2 h. It then displayed the following characteristics: particle size distribution 90% <60 μm; 10% <5 μm; BET surface area 880 m^2/g cat.; the average particle size of Pd evaluated by high resolution transmission electron microscopy (HRTEM) was 5.3 nm, and by H_2 chemisorption was 12.1 nm; the hydrogen uptake (H/Pd) was 0.09. The discrepancy between HRTEM and the adsorption data was attributed to some blockage of the Pd surface by carbon atoms [26].

Preliminary experiments were carried out to test how treatment of the catalyst prior to the reaction would influence the process. We compared the kinetics of the hydrogenolysis of 1,2,4-trichlorobenzene in the presence of the Pd/C catalyst pre-treated by soaking and stirring in *n*-hexane solution with that in the presence of the catalyst pre-treated in 10% aq NaOH. These experiments provided insight into the role of solvent–catalyst interaction in a multiphase system (results – see Fig. 1). It is evident that the Pd/C catalyst pre-treated in the *n*-hexane phase is much more active than the one pre-treated in the aqueous phase – the rate of reaction was ca 38.3× faster. It is very likely that when

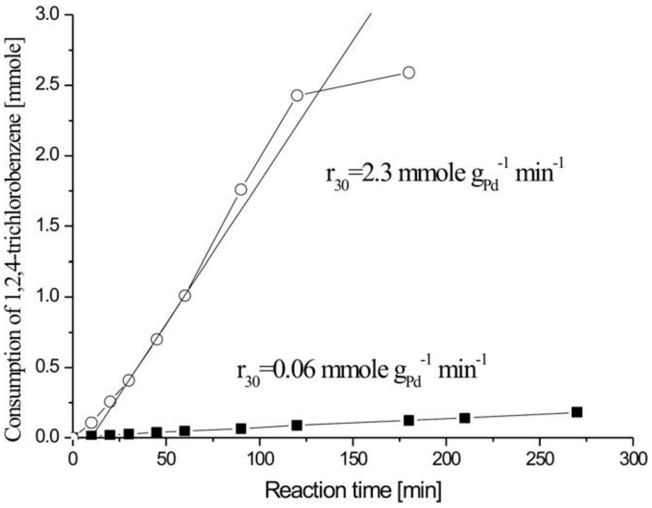

Fig. 1. Variation with time of the amount of 1,2,4-trichlorobenzene consumed during hydrogenolysis over 100 mg 10% Pd/C catalyst in the presence of 10% NaOH and gaseous hydrogen; catalyst in the *n*-hexane phase (○) and the aqueous phase (■). r_{30} – reaction rate after 30 min of the reaction.

the catalyst is coated with the organic solvent, diffusion of the 1,2,4-trichlorobenzene is much better than through the aqueous phase. Thus, all the catalytic experiments were performed with the catalyst soaked in the organic phase.

In separate experiments the influence of the stirring speed (from 700 to 1300 rpm) on the overall reaction kinetics was tested. It was found that the reaction rate increased with stirring speed, reaching a plateau at 1200–1300 rpm. So in our experiments we set the stirring speed at 1300 rpm, which we think was sufficient to minimise the influence of mass transfer on the hydrogenolytic process [14,25]. We therefore adopted the following kinetic model: (a) hydrogen is adsorbed non-competitively on the Pd surface, (b) desorption of benzene and HCl is rapid and does not substantially affect the kinetics of hydrogenolysis, (c) the reaction between hydrogen and aromatic chloride is the slowest process in the system investigated [25].

During hydrogenolysis in an alkaline aqueous-*n*-hexane liquid system with gaseous hydrogen, chlorobenzene produces benzene directly, but di- and tri-chlorobenzenes undergo sequential dechlorination, yielding compounds containing less chlorine. Nevertheless, benzene is always the final product of these reactions.

The results of the dechlorination kinetics obtained in this study are presented in Figs. 2–4 and in Table 1. The initial kinetic rates (r_0) were obtained from the linear fit to the time-dependence of the amount of chlorinated compound during the initial period of the reaction, whereas turnover frequencies (TOFs) were calculated using the initial rates and hydrogen chemisorption data presented in a previous study [26].

First, we investigated chlorobenzene dechlorination under various reaction conditions (Table 1, entries 1–5). Fig. 2 shows the time profile of changes in the amounts of chlorobenzene and benzene during the hydrodechlorination of chlorobenzene with gaseous hydrogen, with and without the addition of 2-methoxyethanol and 2-methoxyethyl ether (diglyme). Some literature reports indicate that 2-methoxyethanol added to the reaction mixture may improve the hydrogenolysis of chloroaromatic compounds [32]. On the other hand, 2-methoxyethyl ether was found to chelate small cations [33]; we presumed this acted as a kind of phase transfer catalyst. In particular, an improvement in the neutralisation of HCl, a reaction by-product deactivating the Pd/C catalyst [26], was expected. The results presented in Fig. 2 and Table 1 (compare entries 1 and 2) show that the addition of 2-methoxyethanol did not change the kinetics of chlorobenzene hydrogenolysis, and no enhancement of the reaction rate was observed. In both cases (with and without the additive), the amount of chlorobenzene decreased linearly with time, suggesting an apparent zero-order kinetic process; after about 60 min most of the chlorobenzene had been dechlorinated. Also, the initial kinetic rates were similar – 3.6 and 3.9 mmole g_{Pd}^{-1} min^{-1} – with and without 2-methoxyethanol respectively. In contrast, the addition of 2-methoxyethyl ether to the reaction mixture did affect the nature of the overall hydrogenolytic process. The changes in the amount of chlorobenzene seem to be exponential, a behaviour that implies apparent first-order kinetics. After 60 min of reaction, only about 50% of the chlorobenzene was dechlorinated (Fig. 2). Presumably, the addition of this compound inhibited to some extent the adsorption of chlorobenzene on the catalyst surface and, contrary to expectations, the dechlorination rate was lower at 1.8 mmole g_{Pd}^{-1} min^{-1} (compare entries 1 and 3). In order to explain the different influence of 2-methoxyethanol and 2-methoxyethyl ether on dechlorination, we performed some additional experiments to test the partition of these compounds between the two phases used. It appears that the former was present almost 100% in the aqueous phase, whereas 70% of the latter was in the aqueous

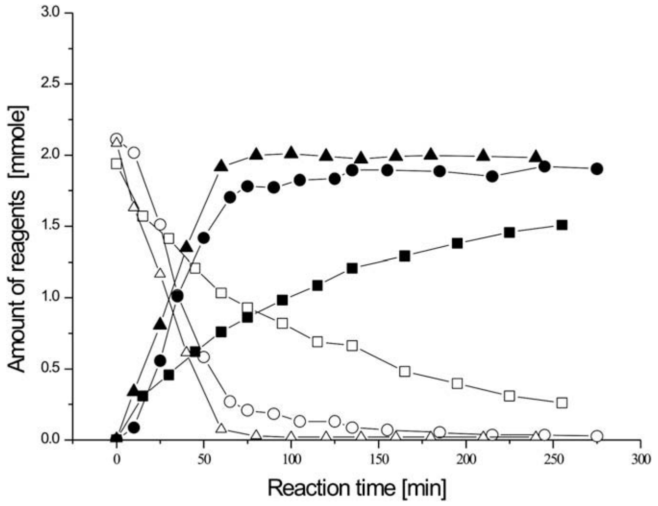

Fig. 2. Variation with time of the amount of chlorobenzene and benzene during hydrogenolysis over 100 mg 10% Pd/C catalyst in the presence of 10% NaOH and gaseous hydrogen; without additives (△,▲), with added 2-methoxyethanol (○,●) and 2-methoxyethyl ether (□,■). The open symbols represent chlorobenzene, the solid symbols stand for benzene.

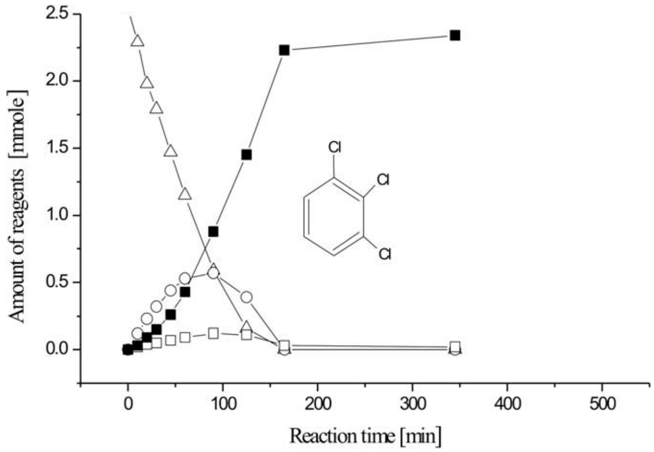

Fig. 3. Variation with time of the amount of 1,2,3-trichlorobenzene (△, 1,2-dichlorobenzene (○), chlorobenzene (□) and benzene (■) during the hydrogenolysis of 1,2,3-trichlorobenzene over 100 mg 10% Pd/C catalyst in the presence of 10% NaOH and gaseous hydrogen.

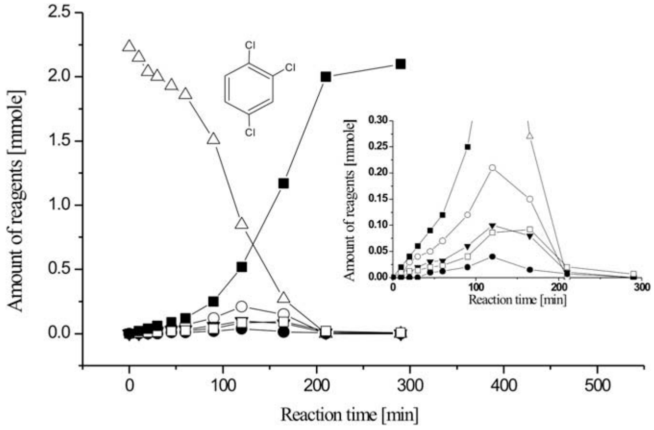

Fig. 4. Variation with time of the amount of 1,2,4-trichlorobenzene (△), 1,2-dichlorobenzene (○), 1,4-dichlorobenzene (●), 1,3-dichlorobenzene (▼), chlorobenzene (□) and benzene (■) during the hydrogenolysis of 1,2,4-trichlorobenzene. Reaction conditions as in Fig. 3. The inset is an enlarged part of the main diagram.

Table 1
Kinetics characteristics of hydrogenolysis of chlorobenzene and some polychlorobenzenes in10% NaOH aq/*n*-hexane in the presence of 100 mg 10% Pd/C catalyst. Hydrogen pressure 1 atm, magnetic stirrer 12 × 5 mm, stirring rate 1300 rpm.

Entry	Compound	Temperature (°C)	Additive	Initial kinetic rate r_0 (mmole g_{Pd}^{-1} min^{-1})	Initial TOF_0 (min^{-1})
1	Chlorobenzene	20	–	3.9	46.7
2	Chlorobenzene	20	2-Methoxyethanol	3.6	43.1
3	Chlorobenzene	20	Diglime	1.8	21.5
4	Chlorobenzene	20[a]	–	7.6[a]	89.4[a]
5	Chlorobenzene	40	–	5.4	63.7
6	1,2-Dichlorobenzene	20	–	2.7	32.3
7	1,2-Dichlorobenzene	20	Diglime	1.8	21.5
8	1,3-Dichlorobenzene	20	–	3.2	38.3
9	1,4-Dichlorobenzene	20	–	2.5	30.1
10	1,2,3-Trichlorobenzene	20	–	2.6	30.3
11	1,2,4 Trichlorobenzene	20	–	0.8	9.4
				2.3[b]	28.0[b]

[a] Reaction performed in the presence of *in situ* generated hydrogen.
[b] Reaction rate r_{30} and TOF_{30} after 30 min run of reaction.

phase and the other 30% in the *n*-hexane phase. Thus, the difference between the effects of the two glycoethers could be due to their different repartition between the two phases used in our catalytic experiments.

Another interesting observation is the large increase in the reaction rate as the hydrogen was switched from gaseous phase to *in situ* generated. This hydrogen was generated in the reaction mixture by the following reaction:

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_2 \quad (1)$$

As shown in Table 1, entry 4, the initial rate of reaction (7.6 mmole g_{Pd}^{-1} min^{-1}) and initial TOF_0 (89.4 min^{-1}) are about twice the values in the presence of gaseous H_2 (entry 1). The reaction rate is also higher than that obtained with gaseous hydrogen at a higher reaction temperature (40 °C, entry 5). In the presence of *in situ* generated hydrogen, the concentration of surface or dissolved hydrogen atoms in the Pd phase is probably greater than that obtained with gaseous hydrogen. The hydrogen atoms dissolved in the Pd crystal are stronger hydrogenating agents than those produced by the dissociation of the gaseous phase molecules at the metal surface [34].

The initial reaction rates for the hydrodechlorination of ortho-, meta- and para-dichlorobenzenes in the presence of gaseous H_2 are presented in Table 1, entries 6–9. The reaction rates and TOFs are slightly lower for these isomers than for chlorobenzene (entry 1). Also, the addition of diglyme decreases the reaction rate (compare entries 6 and 7). The important conclusion is that the position of chlorine in dichlorobenzenes has only a minor influence on the removal of the first chlorine (entries 6, 8, and 9) because the initial kinetic rates are similar, i.e. within experimental error.

Interesting results were obtained for the hydrodechlorination of 1,2,3-trichlorobenzene (Table 1, entry 10, and Fig. 3). This compound undergoes sequential dechlorination with the sorption/desorption of reagents from/to the liquid phase. The initial rate of the elimination of chlorine species is very similar to that obtained for dichlorobenzenes, but the ease of chlorine displacement depends on its position in the molecule. Fig. 3 shows that no measurable quantities of 1,3-dichlorobenzene were detected; the steric effect is therefore clearly in evidence. The 2-chlorine, located between the 1- and the 3-chlorine, either does not undergo hydrogenolysis or else its initial reaction rate is very low. Our results are in full agreement with those reported by Marques et al. [22], who also found a low rate of hydrogenolysis for 2-chloro-1,3-dimethylbenzene.

We also investigated the influence of the position of chlorine in 1,2,4-trichlorobenzene on the susceptibility of this heteroatom to hydrogenolysis (Table 1, entry 11, and Fig. 4). As shown on the inset in Fig. 4, larger amounts of 1,2-dichlorobenzene and 1,3 dichlorobenzene than of 1,4-dichlorobenzene were detected during the hydrogenolysis of this compound. Again, its clear that the reactivity is governed by the position of chlorine in the benzene ring. Inspection of the kinetic hydrogenolysis curves in Fig. 4 shows that the reaction is slow up to 30 min (r_0 = 0.8 mmole g_{Pd}^{-1} min^{-1}), after which the reaction rate increases to r_{30} = 2.3 mmole g_{Pd}^{-1} min^{-1}, a value characteristic of other di and trichlorobenzenes (see Table 1). Additionally, there was hardly any formation of 1,4-dichlorobenzene up to 30 min (see inset in Fig. 4). We may note in passing that the molecular bonds between the carbon and chlorine atoms in polychlorobenzenes are nearly identical. Serguchev and Belokopytov [31] calculated electron densities at the carbon atoms in various chlorobenzenes and detected only small differences in electron densities at the carbons bound to chlorine in dichlorobenzenes, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene. In conclusion, since liquid-phase hydrodechlorination is a stepwise process for the removal of chlorine species, the lower rates of chlorine elimination from position 2, in both 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene, may be related to the inductive and steric effects induced by the benzene–Cl bonds. Similar conclusions can be drawn from the recent study by Meshesha et al. [35], who studied the gaseous-phase hydrodechlorination of 1,2,4-trichlorobenzene over Pd/Mg(Al)O catalysts.

4. Conclusions

Multiphase hydrogenolysis of polychlorinated benzenes over a Pd/C catalyst and gaseous hydrogen is an effective process yielding benzene as the final product. It was found that the effectiveness of the Pd/C catalyst improved in the presence of *in situ* generated hydrogen. The addition of 2-methoxyethanol or 2-methoxyethyl ether to the reaction mixture does not accelerate the dechlorination process.

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